

THE END OF INTERSTELLAR CHEMISTRY AS THE ORIGIN OF NITROGEN IN COMETS AND METEORITES

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ABSTRACT

We describe a mechanism for enhanced nitrogen isotope fractionation in dense molecular gas where most of the molecules containing carbon and oxygen have condensed on grains but where N_2 remains in the gas. The lack of hydroxyl molecules prevents the recycling of N atoms into N_2 , and the nitrogen eventually becomes atomic. Ammonia is formed efficiently under these conditions and rapidly accretes as ice. We find that a significant fraction of the total nitrogen is ultimately present as solid NH_3 . This interstellar ammonia is enhanced in ^{15}N with $^{15}NH_3/^{14}NH_3$ almost 80% higher than the cosmic $^{15}N/^{14}N$ ratio. It is possible that a large part of the nitrogen available to the early solar system was highly fractionated ammonia ice and hence that the ^{15}N enhancements of primitive solar system material and the depletion of N_2 in comets are concomitant. Other implications of this theory for observations of dense molecular material and the nitrogen inventory available to the protosolar nebula are briefly discussed.

Subject headings: comets: general — ISM: abundances — ISM: molecules — meteors, meteoroids — molecular processes

On-line material: color figures

1. INTRODUCTION

The high deuterium fractionation ratios observed in cold molecular clouds, of between 10 and 10,000 times the cosmic D/H value, have led to the identification of the enhanced D/H ratios found in primitive solar system material, such as comets, meteorites, and interplanetary dust particles (IDPs), with an interstellar provenance (e.g., Messenger & Walker 1997; Ehrenfreund & Charnley 2000). Low-temperature gas-phase ion-molecule reactions and catalysis on cold interstellar dust grains both lead to molecules fractionated in D (e.g., Millar et al. 2000; Tielens 1983; Charnley, Tielens, & Rodgers 1997).

Some meteoritic materials and IDPs also possess enhancements and anomalies in their $^{15}N/^{14}N$ ratios. The lack of any significant ^{13}C enhancement in the material with the largest ^{15}N content rules out a nucleosynthetic origin for the nitrogen fractionation and suggests that, as with deuterium, the ^{15}N -rich material results from low-temperature interstellar chemistry (Kerridge, Chang, & Shipp 1987; Messenger & Walker 1997; Alexander et al. 1998). Despite the common belief that significant ^{15}N fractionation could occur in interstellar chemistry, until recently there had been little work on this problem (Adams & Smith 1981). An important advance was made by Terzieva & Herbst (2000), who calculated the exoergicity of a variety of potential fractionation reactions. In a dark-cloud chemical model, Terzieva & Herbst found that the enhancements in ^{15}N were modest, reaching a maximum of ~25% early in the calculation.

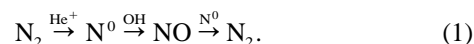
Although there is evidence for an “interstellar” D/H ratio in an IDP (Messenger 2000), the D/H ratios measured in most primitive solar system material are typically at the lower end of what is found in interstellar molecules. Processing of interstellar material in the protosolar nebula may have lowered the original D/H ratios, and this suggests that the nitrogen fractionation of the original material could also have been larger than is presently found. In this Letter, we show that gas-grain effects could lead to significant ^{15}N fractionation. Very specific conditions are required for this to occur, and we also discuss

the implications of these for the origin of nitrogen in the solar system.

2. THEORY

In high-density molecular cores, or in the outermost regions of protostellar disks, molecular depletion onto 10 K dust grains can play an important role in enhancing chemical fractionation. It is well known that when significant depletion occurs, the D/H ratios of the remaining gas-phase species can be enormous (~0.1–1) because there are fewer heavy molecules available to remove H_2D^+ (see Millar et al. 2000; Tiné et al. 2000; Rodgers & Charnley 2001b).

A different mechanism can operate for nitrogen isotope fractionation. Under normal interstellar conditions, N_2 is the dominant form of nitrogen and ^{14}N and ^{15}N atoms are continuously cycled through the sequence



The first step of reaction (1) also produces N^+ , which reacts with H_2 and leads to ammonia. In this situation the fraction of gas-phase nitrogen in the forms N^0 , N^+ , and N_2H^+ is small, and since reactions involving these species are most important for fractionation, the resulting ^{15}N enhancements are modest (Terzieva & Herbst 2000). There is growing observational evidence that in the high-density environment of protostellar cores, CO may be selectively depleted in CO ice relative to both H_2 and N_2 (Mauersberger et al. 1992; Caselli & Walmsley 2002; Bergin et al. 2001), and models of this effect have been developed (e.g., Charnley 1997). If O/C-bearing molecules, mainly CO, are depleted from the gas, there is insufficient OH to drive the above cycle, and this leads to more nitrogen atoms being freed from N_2 . The large abundances of ^{14}N and ^{15}N atoms in the gas then partake in a very restrictive chemistry. The subsequent fate of ^{15}N atoms in ultradense material requires that N atoms, like N_2 molecules, do not stick efficiently to grains, consistent with the available experimental evidence (e.g., Tielens & Allamandola 1987).

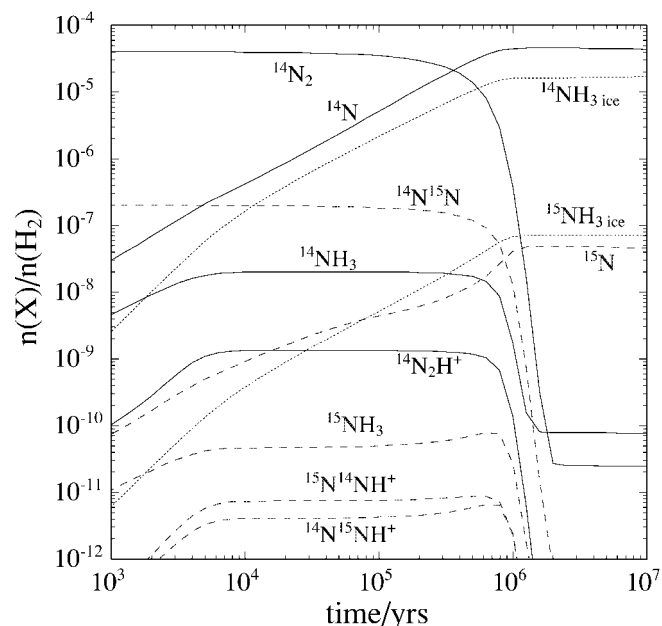


FIG. 1.—Abundance vs. time of N-bearing molecules and their isotopomers in a cold dense cloud ($n = 10^7 \text{ cm}^{-3}$; $T = 10 \text{ K}$), with all species except H_2 , N_2 , and atoms accreting onto grains. Decline in the N_2 abundance is due to reactions with He^+ . [See the electronic edition of the Journal for a color version of this figure.]

We have calculated the time-dependent nitrogen isotopic ratios attainable in such an accretion-dominated chemistry by modifying the model of Charnley (1997) to include the ^{15}N fractionation reactions of Terzieva & Herbst (2000) for the N_2 and NH_3 chemistries. Although we initially consider this effect in the context of dense prestellar cores, as we discuss in § 4 below, results from this model should also be relevant for the chemistry in the cold outer regions of protostellar disks (see Charnley 1995). Briefly, this model considers the gas-grain chemistry in high-density cores that have formed quasi-statically in molecular clouds, before the onset of dynamic gravitational collapse (see Brown, Charnley, & Millar 1988). The timescale for these cores to evolve to the state where we begin the calculation is longer than a million years, after which time molecules should be only slightly enriched in ^{15}N (Terzieva & Herbst 2000).

In the calculation, the gas phase is almost fully molecular, and initially it is assumed that species are present in the gas with normal, observed or calculated, interstellar abundances. We assume that some, as yet unidentified, nonthermal desorption process has maintained CO and N_2 , as well as all the heavy atoms, in the gas (see Willacy & Millar 1998 for a review). This desorption is molecule-dependent and according to the relative volatilities of the species (i.e., $\text{CO} < \text{N}_2 < \text{C}^0, \text{O}^0, \text{N}^0$; see Tielens & Allamandola 1987). Positive ions are assumed to be neutralized on negatively charged grains and returned to the gas. The cosmic-ray ionization rate, ζ , controls the production rate of He^+ and hence the timescale for N_2 destruction; we used a value of $\zeta = 5 \times 10^{-17} \text{ s}^{-1}$. We adopt a gas density of 10^7 cm^{-3} and a temperature of 10 K for the gas and dust. The material then undergoes a small increase in density such that *only* CO desorption is unable to compete with accretion, and we then follow the gas-grain chemistry.

3. RESULTS

Figure 1 shows the time variation of the abundances of N-bearing species; it is apparent that on a timescale of a few times

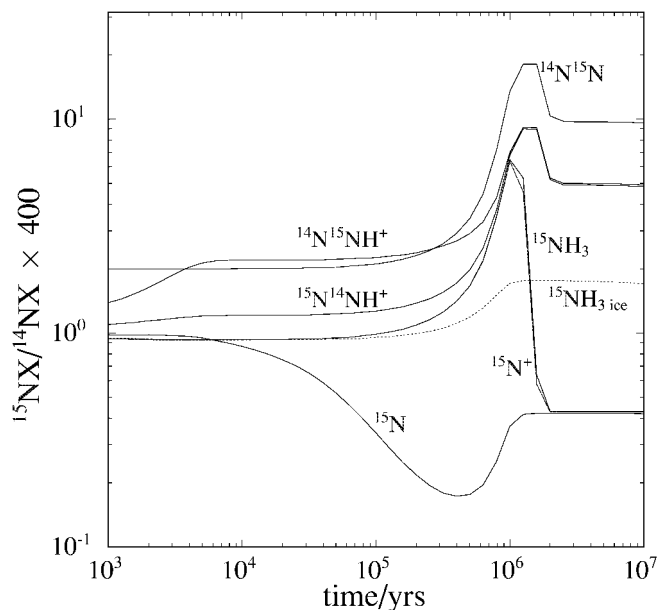
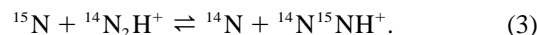
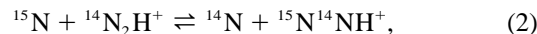


FIG. 2.—Relative fractionation of ^{15}N in different species. Initial $^{14}\text{N}/^{15}\text{N}$ ratio is assumed to be 400. [See the electronic edition of the Journal for a color version of this figure.]

10^5 yr , molecular nitrogen is broken down into atoms. It is also clear that large abundances of ammonia are formed that freeze out onto grains. Figure 2 shows the relative fractionation of ^{15}N in different species. The relatively low amount of ^{15}N in atomic form is due to two exchange reactions with $^{14}\text{N}_2\text{H}^+$:



When $^{14}\text{N}^{15}\text{NH}^+$ and $^{15}\text{N}^{14}\text{NH}^+$ undergo electron dissociative recombination, this excess fractionation feeds back into $^{15}\text{N}^{14}\text{N}$, which in turn causes an excess of $^{15}\text{N}^+$, leading to fractionation of $^{15}\text{NH}_3$. Hence, when the chemistry reaches quasi-steady state, ^{15}N is preferentially incorporated into gas-phase N_2 and solid NH_3 , whereas atomic N—which accounts for almost all the gas-phase nitrogen—is depleted in ^{15}N . Figure 2 shows that the $^{15}\text{NH}_3/^{14}\text{NH}_3$ ratio in the ices is about 1.8 times the interstellar $^{15}\text{N}/^{14}\text{N}$ value adopted (1/400; Dahmen, Wilson, & Matteucci 1995). Calculations using different overall $^{15}\text{N}/^{14}\text{N}$ ratios (Kallenbach et al. 1998; Fouchet et al. 2000) produced no discernible effect on the fractionation shown in Figure 2. Terzieva & Herbst (2000) also considered fractionation reactions driven by N^+ , as well as isotope exchange reactions involving N_2H^+ and N_2 (Adams & Smith 1981). We found that these reactions do not result in such appreciable fractionation. We therefore conclude, as did Terzieva & Herbst, that reactions (2) and (3) are the most important routes to ^{15}N fractionation in cold gas. Their influence on fractionation will be most pronounced in regions where a large portion of the nitrogen is in atomic form; models in which atoms were allowed to freeze out onto grains produced no significant fractionation.

We have shown the simplest case of the evolution in static gas going to the complete dissociation of N_2 , where only the ammonia ices display ^{15}N enhancements coupled with a large absolute abundance. In reality, there will be a dynamical-chemical evolution (Brown et al. 1988), and so the fractionation chemistry may be terminated at some earlier time. There are two

possible cases. As the accretion-desorption balance of a molecule at a given density determines the amount of gas-phase depletion, a subsequent increase in density will lead to first N_2 and then N atoms also freezing out on grains. If this occurs at some reference time, say t_0 , then the chemical state of the gas at t_0 will effectively determine the mantle composition. If $t_0 \geq 8 \times 10^5$ yr, then highly fractionated N_2 could be added to the mantles. In this case only a fraction ($\sim 20\%$) of the original nitrogen is in solid molecular form; the remainder is in gaseous atoms. If the density increases further, such that N atoms accrete and are reduced to ammonia, the enhanced $^{15}N/^{14}N$ fractionation in ammonia will be greatly diluted to a value closer to the elemental ratio. This leads to mantles in which now only the N_2 contains an enhancement in ^{15}N , the amount of which depends upon t_0 . However, in either dense cores or protostellar disks, the physical effect most likely to terminate the cold core evolution at some t_0 is simply a rise in the dust/gas temperature. Even a very modest rise in the gas temperature to ≈ 15 – 20 K will greatly reduce the efficiency of the ^{15}N fractionation reactions, and as the gas and dust are thermally well coupled, CO desorption at dust temperatures in excess of 20 K leads to consumption of N atoms by the resumption of the cycle (1).

4. DISCUSSION

We now consider the implications of this theory for interstellar chemistry and the nitrogen inventory of primitive solar system material.

4.1. Interstellar Chemistry

The simplest models of hot core chemistry assume that all the heavy molecular material freezes out completely in the cold phase (e.g., Brown et al. 1988). Selective molecular depletion means that some hot cores could have had large initial N^0/N_2 ratios. In such cores the chemical timescales required to form various nitriles will be much shorter, and some of the discrepancies that arise when trying to chemically date hot cores may be alleviated (Rodgers & Charnley 2001a). The large ammonia abundances observed in hot cores could be formed by either reduction of N atoms on cold grains (e.g., Brown et al. 1988) or hot gas-phase reactions (Rodgers & Charnley 2001a). Figure 1 shows that high abundances of solid ammonia may also be formed in the depletion phase without surface reactions. The presence of ammonia-rich ices toward protostars is controversial at present with low NH_3/H_2O ratios indicated (see Gibb, Whittet, & Chiar 2001). One possible explanation of this discrepancy is that formation of abundant ammonia ice is a transient event ($\sim 10^5$ yr) that occurs only in the innermost regions of the cold core. As these regions subsequently become the hottest, their ices are completely evaporated, and hence the resulting protostellar core comes to possess little NH_3 ice in the cooler outer envelope but a large abundance of NH_3 in the innermost regions.

Observations of *massive* star-forming regions are at least consistent with emission from selectively depleted cores (Fig. 1). The isotopomers of N_2H^+ are most easily detected toward them (Womack, Ziurys, & Wyckoff 1992b), and N_2 appears to be less abundant when compared to dark clouds (Womack, Ziurys, & Wyckoff 1992a). We also note that in the original detection of these isotopomers in DR 21(OH), Linke, Guélin, & Langar (1983) suggested that they originated in gas with depleted CO and $N_2/CO \sim 1$. In *low-mass* cores the general applicability of the theory is observationally less clear. Selective depletion can account for the removal of CO and CS, while maintaining N_2H^+ and NH_3 in the gas (Bergin & Langer 1997; Charnley 1997),

but maps of N_2H^+ (Williams et al. 1999) and NH_3 emission do not show a characteristic “gap” evident in, e.g., CS and CCS relative to NH_3 (e.g., Willacy, Langer, & Vellusamy 1998). This may indicate that in general, low-mass cores do not complete the depletion chemistry shown in Figure 1. However, as significant N_2 destruction is necessary to reach the highest $^{15}N/^{14}N$ ratios required by the meteoritic data, it may indeed have occurred, at least once, in regions of the protosolar core. To be less sanguine, estimates indicate that the depletion phase of low-mass star formation lasts only a time shorter than needed to reach these $^{15}N/^{14}N$ ratios (van Dishoeck et al. 2002); a lower value of ζ in our model would exacerbate this problem. Also, it is uncertain whether high-density cores could be sustained long enough against collapse. Accepting this mechanism as the origin of the meteoritic anomalies, the depletion chemistry may be more likely to occur in the cold outer regions of the protosolar disk, where cometsimals were assembled and longer evolutionary timescales are available for the chemistry. Nevertheless, we predict that in dark clouds that exhibit CO depletion, such as L1498, L1544, and IC 5146 (Willacy et al. 1998; Caselli & Walmsley 2002; Bergin et al. 2001), the abundances of both $^{14}N^{15}NH^+$ and $^{15}N^{14}NH^+$ should be enhanced.

4.2. Solar System Material

Irrespective of whether the chemistry in Figure 1 occurred in a dense core or a disk, this theory suggests that three problems with the nitrogen inventory of the early solar system are intimately connected.

4.2.1. Comets

Recent observations of interstellar water and atomic oxygen (Melnick et al. 2000; Caux et al. 1999) are consistent with the ices formed from this gas phase having abundances relative to hydrogen of $x(H_2O) \sim a \text{ few } \times 10^{-4}$. We predict solid ammonia abundances of $x(NH_3) \sim 10^{-5}$. Cometary NH_3/H_2O ratios are typically $\sim 1\%$ – 3% , and so our predicted mantle composition is consistent with these ices ultimately being incorporated in comets.

Our calculations suggest an alternative to volatile sublimation as the origin of the observed widespread depletion of N_2 in comets (Cochran, Cochran, & Barker 2000): a significant fraction of the original interstellar N_2 was destroyed before incorporation in icy cometsimals. The total population of N-bearing molecules in *solid form* available to the forming solar system was less than the total elemental nitrogen initially present (as N_2) in the protosolar core. This may explain why the overall elemental N/O ratio in comet Halley dust appeared to be depleted in the nitrogen component relative to the solar value (Irvine et al. 2000).

Assuming interstellar material was first incorporated in the solar nebula relatively unscathed, then if only a few percent of the original interstellar N_2 was available (as gas or ice), an important issue concerns the fate of the $N^0/N_2/NH_3$ ratios deposited in the comet-forming regions of the nebula, particularly the nitrogen atoms. If N atoms freeze on grains and are reduced, then comets would have $NH_3/H_2O \sim 10\%$ or more and would show no overall N/O depletion relative to the solar ratio. We tend therefore to discount this possibility. It is most likely that N atoms do not freeze out and are converted to N_2 by warm chemistry in the inner nebula (e.g., Fegley & Prinn 1989) and by the resumption of the sequence (1) in the weakly ionized outer nebula. This nebular N_2 could in principle become incorporated into precometary ices and then be evaporated later to reproduce the observed N_2 depletion (see Owen & Bar-Nun

1995). However, our results indicate that cometary ices can contain a small fraction of the original N_2 without them ever having to experience temperatures above about 20 K. Ammonia ice can be retained up to ~ 80 K (e.g., Mumma, Weisman, & Stern 1993; Sandford & Allamandola 1993), and such high $^{15}NH_3/^{14}NH_3$ ratios could easily be preserved on comet-forming grains since, for example, the detection of argon in comet Hale-Bopp indicates its ices never experienced heating above 35–40 K (Stern et al. 2000).

Recently, Kawakita et al. (2001) inferred a formation temperature of ≈ 28 K for the ammonia ice in comet C/1999S4 LINEAR. This is clearly inconsistent with selective depletion but also with other observations that indicate a warmer formation site for this particular comet (Mumma et al. 2001). It would be interesting to know, for a sample of comets, how the NH_3 formation temperature, derived from the NH_2 ortho-para ratio, compares to the ^{15}N fractionation.

4.2.2. Meteorites

Unspecified isotopic effects resulting from the differing volatilities of H_2 , N_2 , and CO were noted by Messenger & Walker (1997) as possibly being responsible for the low ^{13}C enrichment in meteorites relative to D and ^{15}N . Selective depletion indicates that the major reservoir of ^{15}N nuclei in the early solar system was ammonia ice. The enhancement of ^{15}N in solid ammonia of $\sim 80\%$ is more than sufficient to explain the ^{15}N enrichment found by Messenger (2000) in the IDP “dragonfly” of $\sim 50\%$. For comparison, the closest values found by Terzieva & Herbst (2000) were $\sim 25\%$. The ^{15}N anomalies in meteorites appear to be correlated with the deuterium enrichment and lie in the carbonaceous component. If ammonia comprised most of the initial nitrogen inventory that was eventually processed into meteoritic material, then another level of solid-state processing is required, one that allows this reservoir to become incorporated into the coexisting deuterated organic component. One possibility is that ultraviolet photolysis or heavy particle bombardment attached $^{15}NH_2$ groups to organics embedded in the ices, to either simple species or more complex refractory ones, such as polycyclic aromatic hydrocarbons (PAHs; Sandford, Bernstein, & Dworkin 2001). One attraction of this scenario is that ices containing PAHs and ammonia can be retained and

modified over a wider range of temperatures than, e.g., would be the case if N_2 were the major ^{15}N reservoir.

5. CONCLUSIONS

We have demonstrated a mechanism whereby ion-molecule chemistry in dense interstellar and/or protostellar material could produce much larger $^{15}N/^{14}N$ fractionation in specific interstellar molecules than previously calculated (see Terzieva & Herbst 2000). The conversion of gaseous N_2 to nitrogen atoms and ammonia ice provides an alternative explanation for the early chemical state of star-forming cores.

Previous work has assumed that almost all the nitrogen initially available to the early protosolar nebula was N_2 (e.g., Irvine et al. 2000). We have shown that it is possible that much of the gaseous and solid nitrogen available was atomic nitrogen and highly fractionated ($\sim 80\%$) ammonia ice, with probably a smaller admixture of solid N_2 . Ammonia ice production, ^{15}N enhancement, and N_2 depletion are concomitant processes. This further strengthens the idea that comets are the precursors of some IDPs and meteoritic material. In particular, this ammonia ice could account for the ^{15}N enrichments found in meteoritic amino acids if they indeed formed by Strecker-cyanohydrin synthesis (e.g., Cronin & Chang 1993). This theory also suggests that the *solid* nitrogen component of primitive solar system material should show a lower overall N/O ratio than the solar value. A discussion of the wider implications for the chemistry of the early solar system and the relation to planetary atmospheres is beyond the scope of this Letter (see Owen et al. 2001; Owen & Bar-Nun 2001). An understanding of how physical processes in cold outer regions of the protosolar disk affect the precise gaseous and solid-state abundance ratios and fractionation requires more detailed modeling (e.g., Aikawa & Herbst 2001).

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